11th International Seminar on the Commercial Applications for Inherently Conductive Polymers
Pittsburgh, October 6-7 2004

Solvent Processable Conducting Block Copolymers Based On Poly(3,4-ethylenedioxythiophene)

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Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **OCT 2004**	2. REPORT TYPE	3. DATES COVERED **00-00-2004 to 00-00-2004**

4. TITLE AND SUBTITLE **Solvent Processable Conducting Block Copolymers Based on Poly(3,4-ethylenedioxythiophene)**	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **TDA Research Inc,12345 West 52nd Avenue,Wheat Ridge,CO,80033-1916**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
The original document contains color images.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**		**26**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

Acknowledgements

- Shawn Sapp
- Emily Chang
- Carolina Wilson
- Raechelle D'Sa
- Brian Elliott
- Wallace Ellis

- NSF
- Air Force
- NIH
- TDA Research

TDA Research

TDA Research

- Began operations in 1987
- 65 Full-time technical staff
- $ 9.6 Million annual revenue
- 50,000 ft^2 Total facility

- Performs contract R&D
- 15 patents, 29 pending applications
- Commercializes technology by
  - Internal business units
  - Joint ventures
  - Licensing

Outline

- Problems with ICP commercialization
- Processing: current approaches
- TDA's approach
- PEDOT-PEG block copolymers
- Other conducting block copolymers
- Concluding remarks

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ICPs in Numbers

- Discovered in the late 70's
- Ten thousands of scientific papers published since discovery
- Some 40,000 patents filed since 1976
- Nobel Prize awarded in 2000
- Only a few commercial applications with limited markets
- North America ICP sales were $140 million in 2003 and are projected to be $610 million in 2008 (Conductive Polymers, BCC Report 2003)

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ICP Problems

1. **Metallic conductivity is difficult to achieve**
2. **Dark in color**
3. **Poor long-term and thermal stability**
4. **Difficult processing**
   - Rigid rod chains
     - DON'T FLOW & DON'T MELT
   - Poly(ionic) chains with intercalated counterion
     - DON'T DISSOLVE

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TDA's Objectives

- **Develop new practical processing methods for existing ICPs**
- **Increase versatility and global use of ICPs**
- **Focus on PEDOT:**
  - Offer a range of solvents
  - Avoid a large excess of polyelectrolyte
  - Reduce hygroscopic and acidic properties
- **Also polypyrrole:**
  - Stimuli-responsive biodegradable biomaterial

Current ICP Processing Methods

- From undoped state / post processing doping
- *In Situ* polymerization
- Fancy solvents, cosolvents, dopants
- Oligomer approach
- Dispersion techniques

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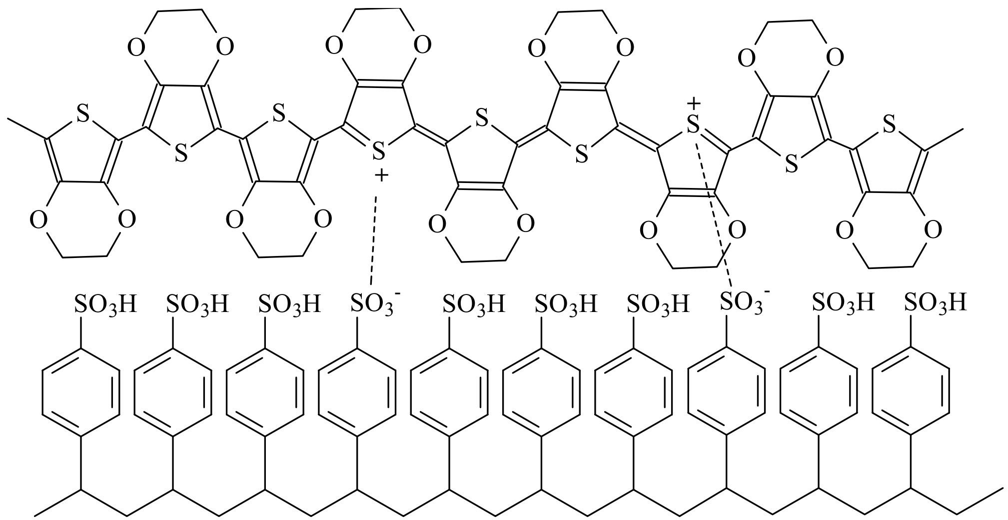
PEDOT/PSS Dispersion (Baytron® P)



Ionic-Stabilized Water-Based Dispersion

- **Large excess of PSSH**
- **Hygroscopic, acidic, corrosive**
- **Poor wetting of organic substrates**
- **Difficult to blend with hydrophobic resins and polymers**

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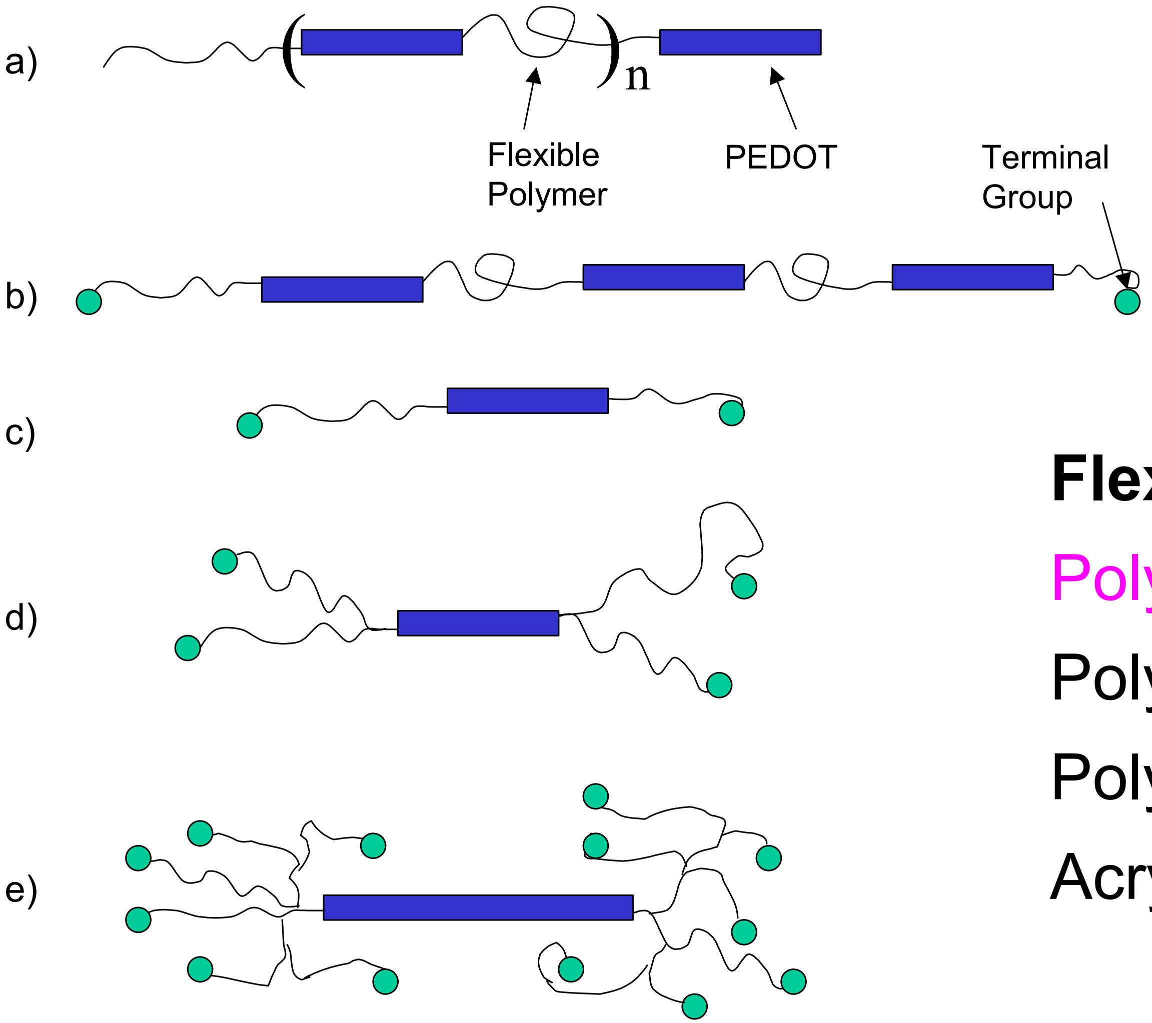
TDA's Approach: Block Copolymers & Capped Oligomers

US Patent Application US2003/0088032 A1



Steric-Stabilized Solvent-Based Dispersions

Flexible segments:

Poly(ethylene glycol)

Poly(propylene glycol)

Poly(dimethylsiloxane)

Acrylates

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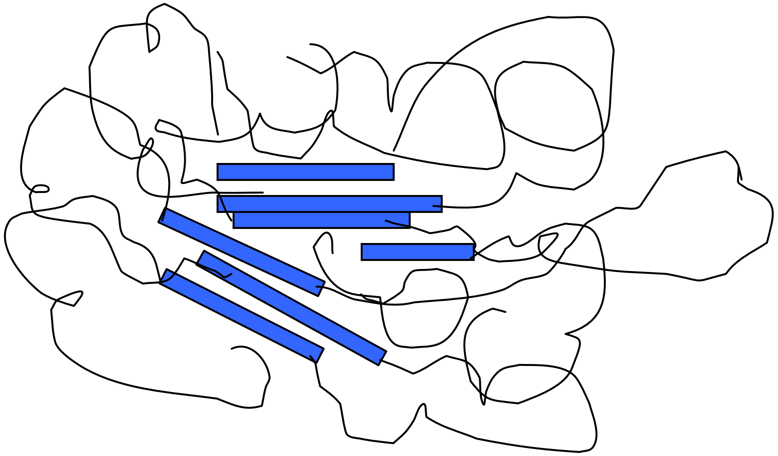
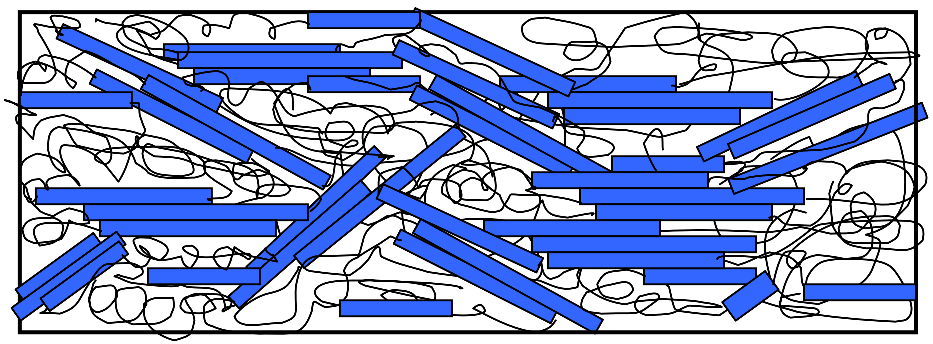
Solution and Solid State Structures



Steric-stabilized colloidal dispersion in solution



Phase-separated domains in solid state

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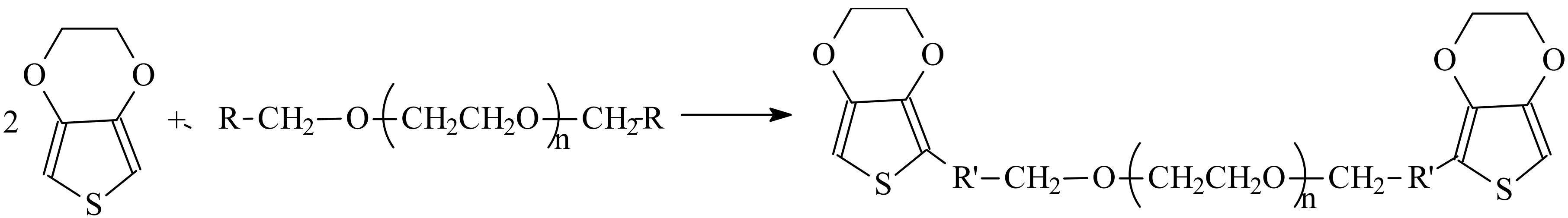
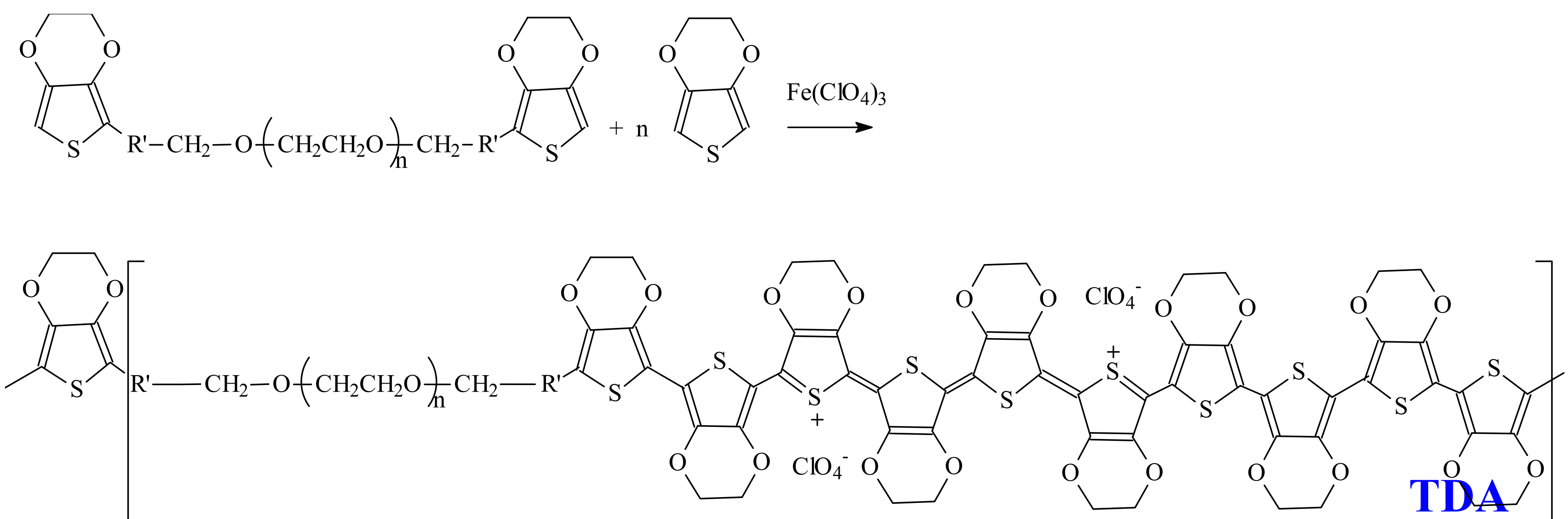
PEDOT-PEG Copolymers Synthesis

1) Synthesis of Polymerizable Macromonomers



2) Oxidative Polymerization



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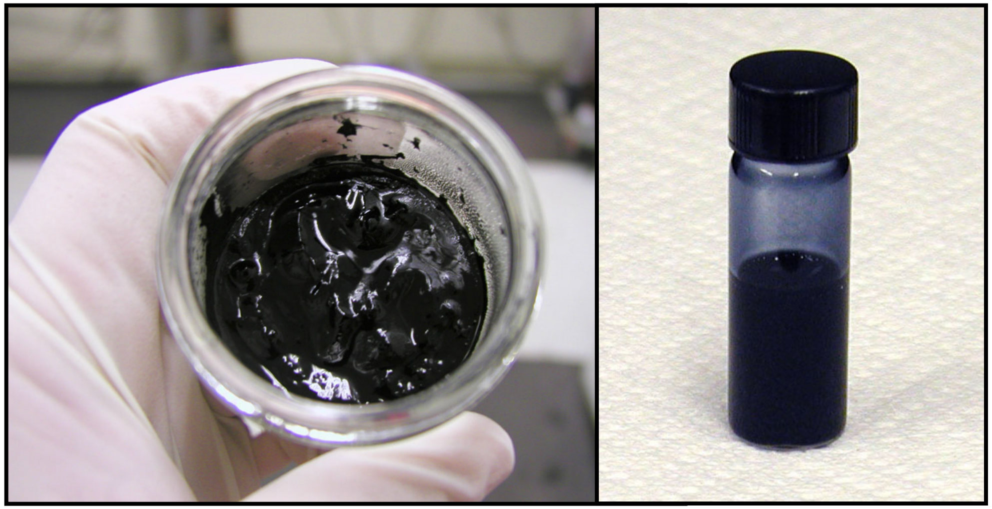
Purification and Dispersion



Sample Description	Chlorine Content (ppm)	Iron Content (ppm)
raw product	6310	3410
first rinse	2900	700
second rinse	2200	100
third rinse	2310	19

Doping level ≅ 24% based on # of EDOT units

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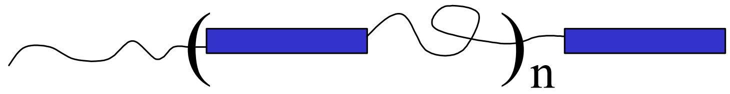
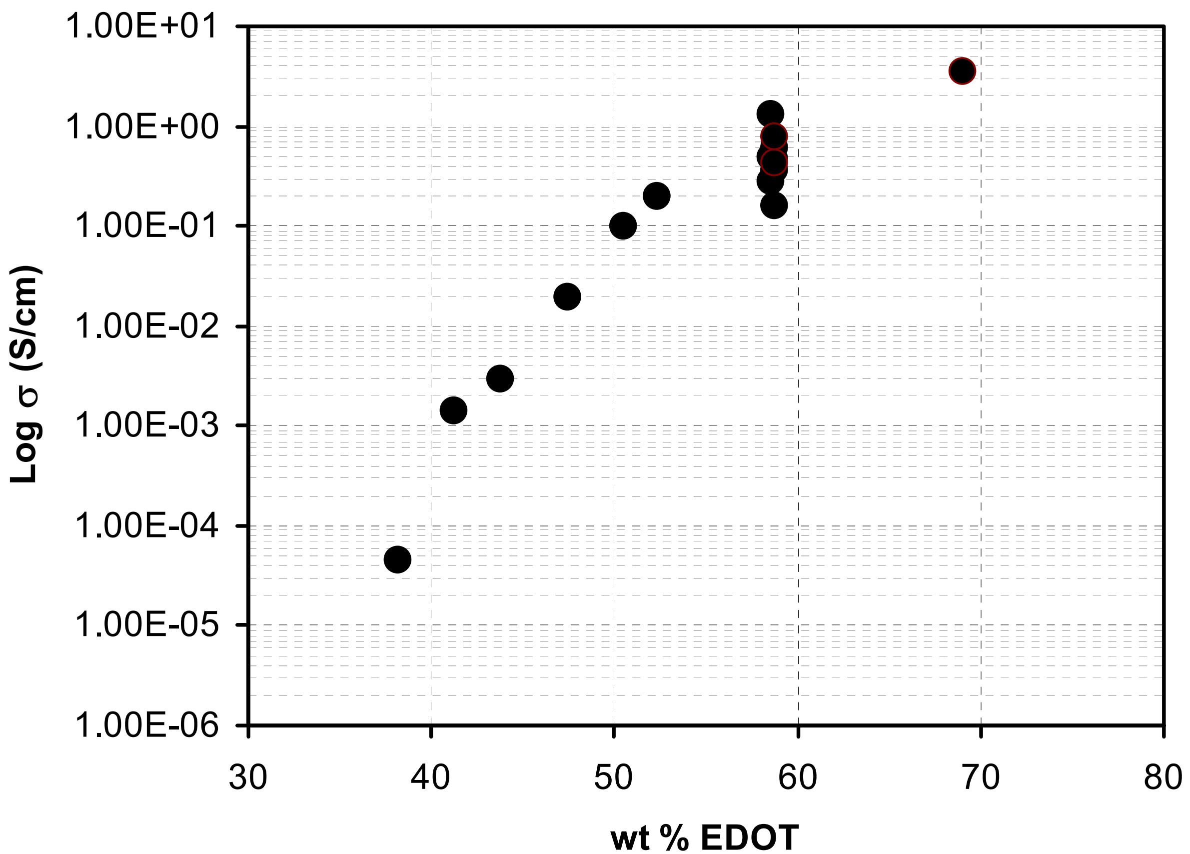
Linear Copolymers: Conductivity Versus PEDOT/PEG Ratio





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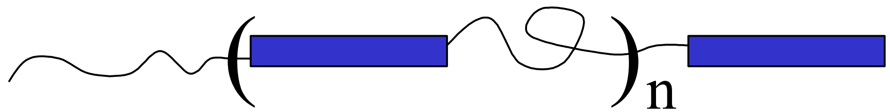
Linear Copolymers: Conductivity Versus Dopant



- **Perchlorate doped copolymer:**
  $\sigma = 10^{-1}\text{-}10^{0}$ S/cm

- **Triflate doped copolymer:**
  $\sigma = 10^{-2}$ S/cm

- ***Para*Toluensulfonate doped copolymer:**
  $\sigma = 10^{-4}\text{-}10^{-3}$ S/cm

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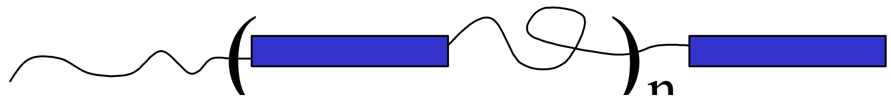
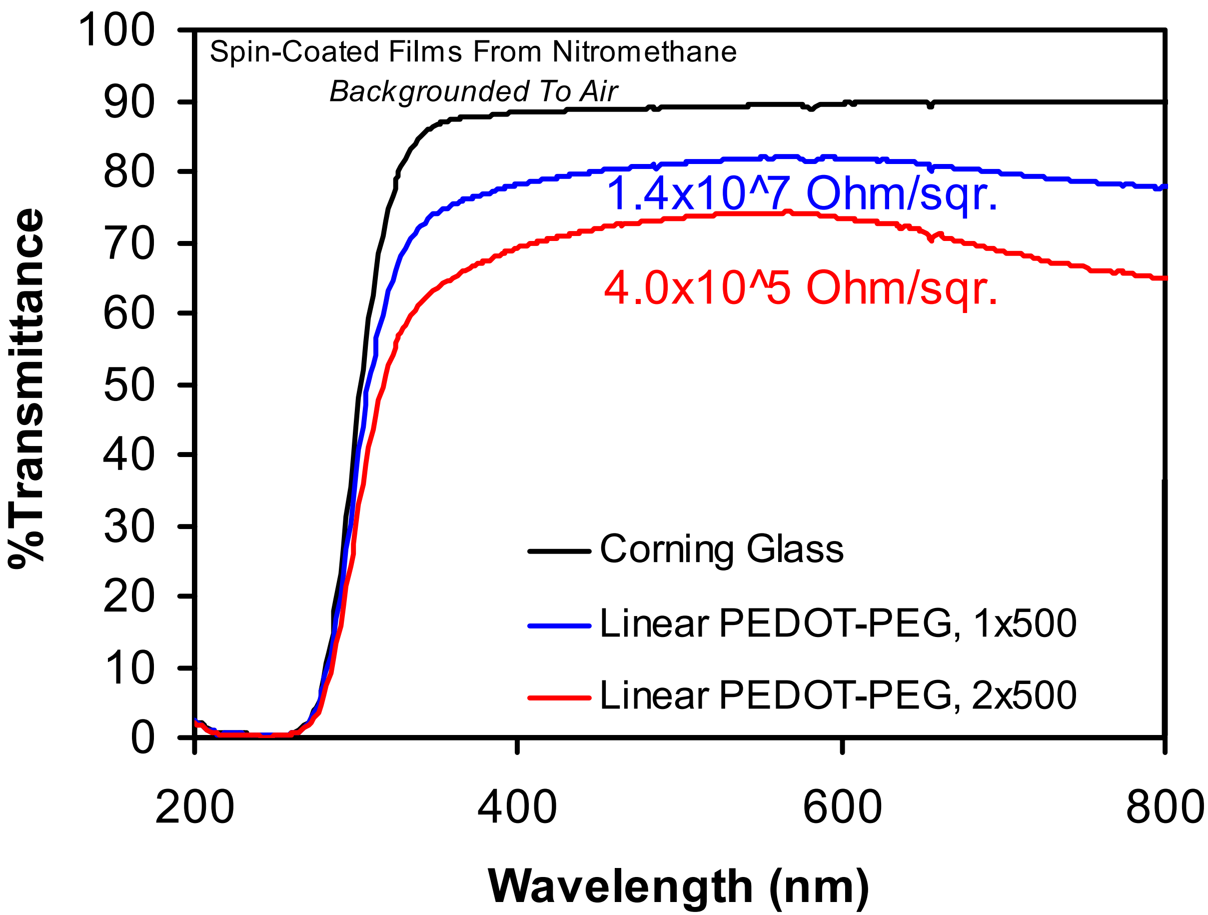
Linear Copolymers: Optical Clarity





Bulk Conductivity
0.4 S/cm

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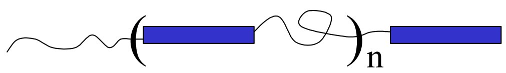
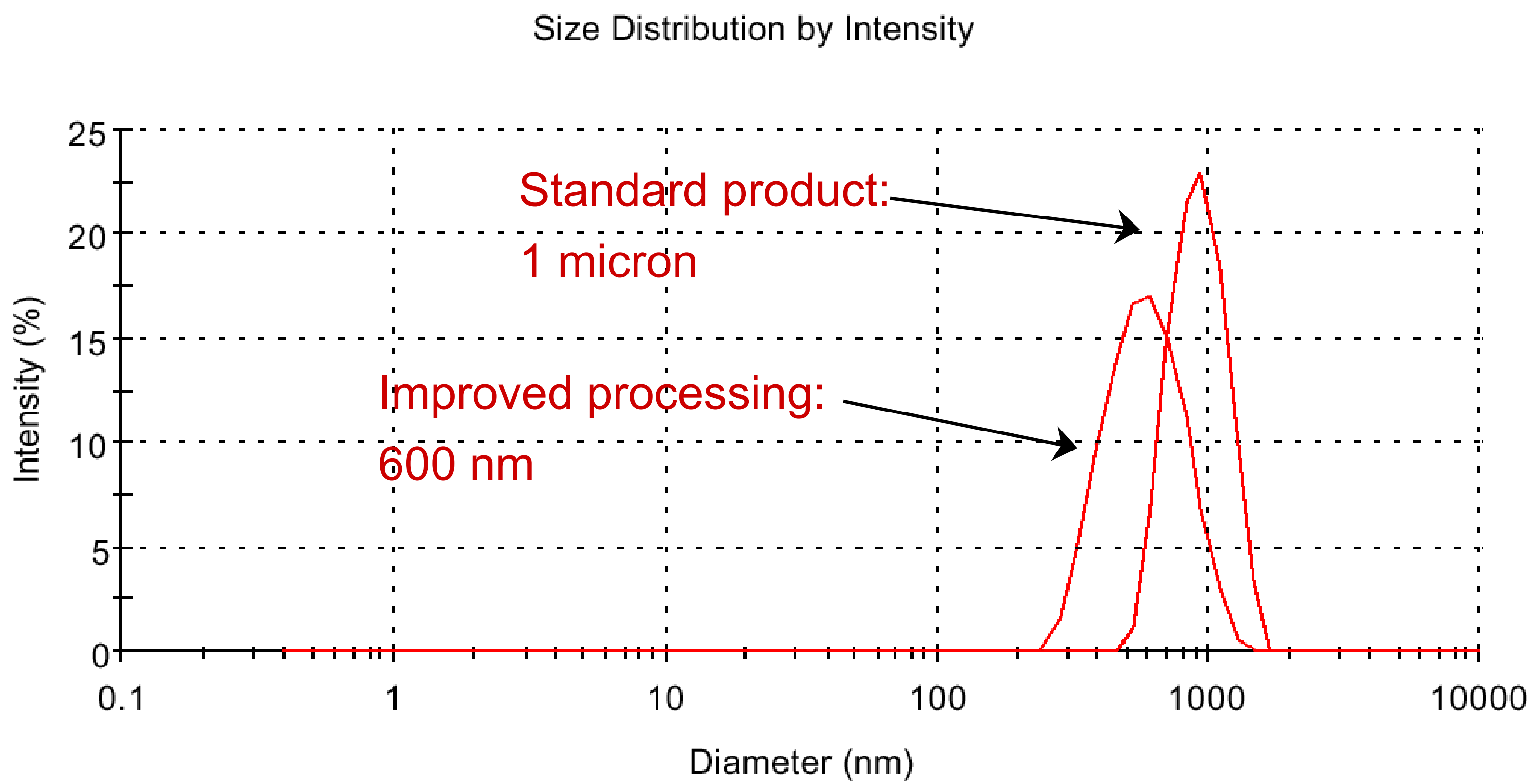
Linear Copolymers: Particle Size





Light Scattering of Solvated Colloidal Particles

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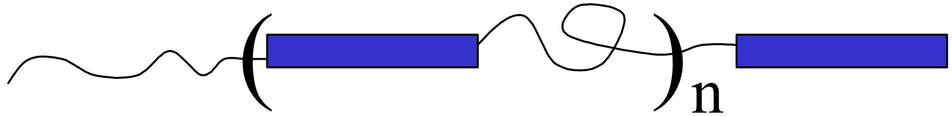
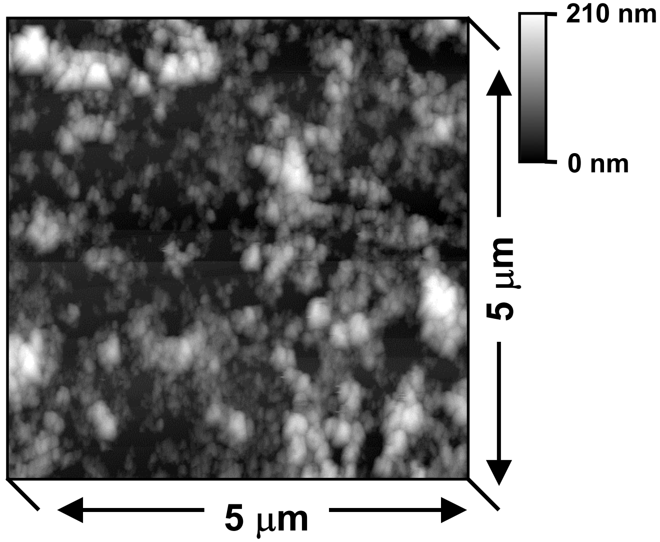
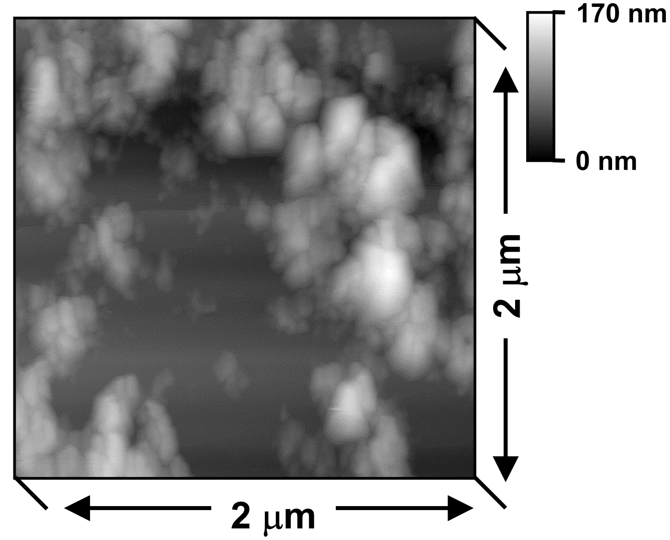
Linear Copolymers: Surface Roughness



RMS Roughness = 42.9 nm
Avg. Roughness = 31.8 nm



RMS Roughness = 36.5 nm
Avg. Roughness = 30.0 nm



Contact Mode AFM: dry film on float glass

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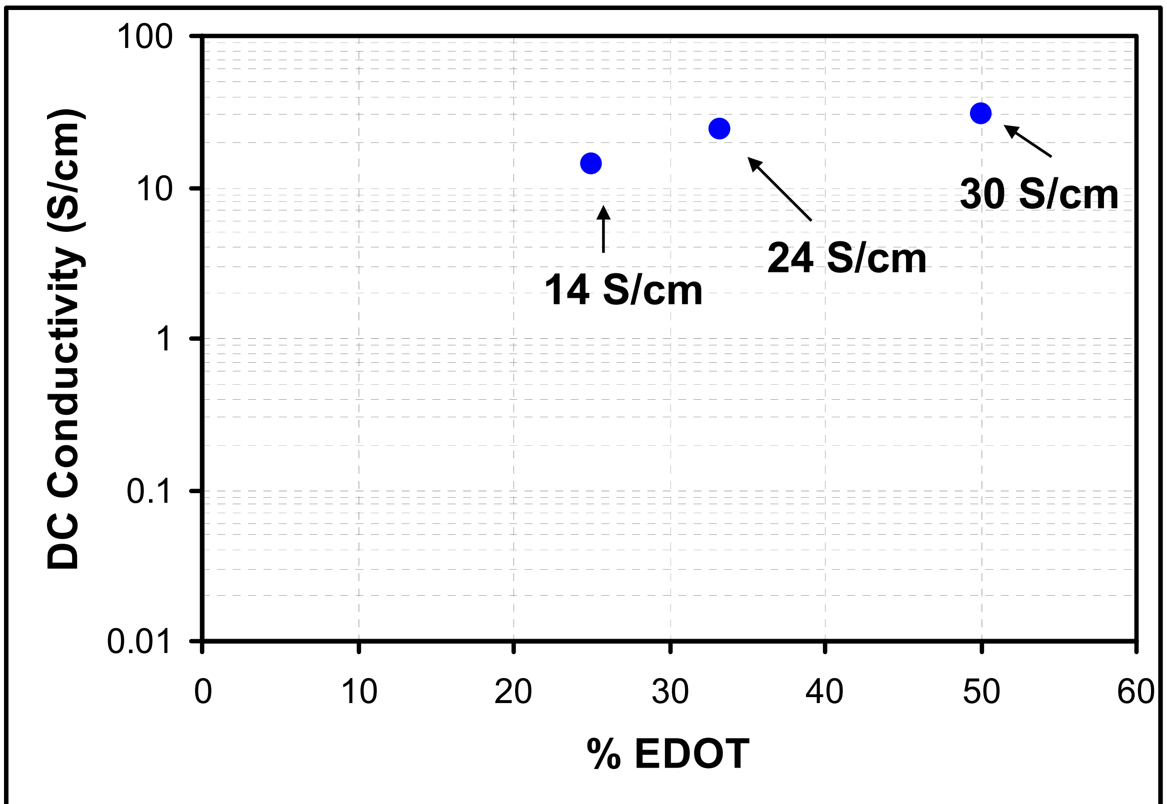
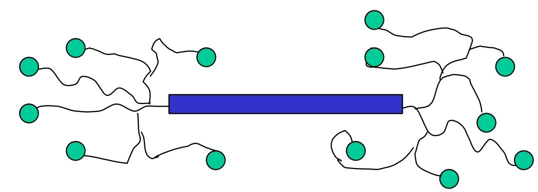
Hyperbranched Copolymers: Conductivity Versus Composition





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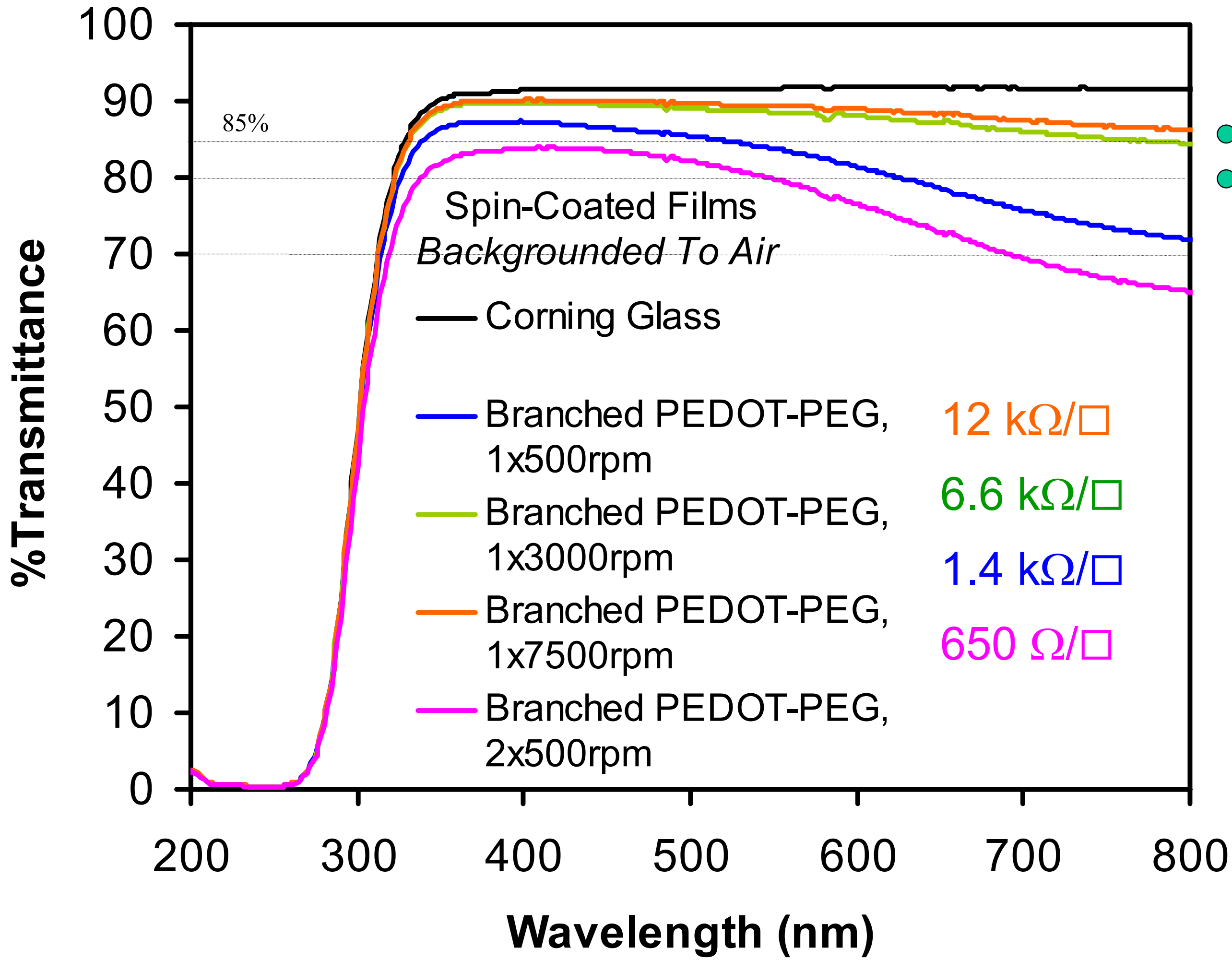
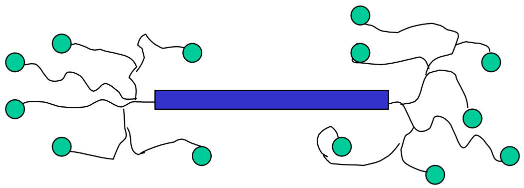
Hyperbranched Copolymers: Optical Clarity





Bulk Conductivity
14 S/cm

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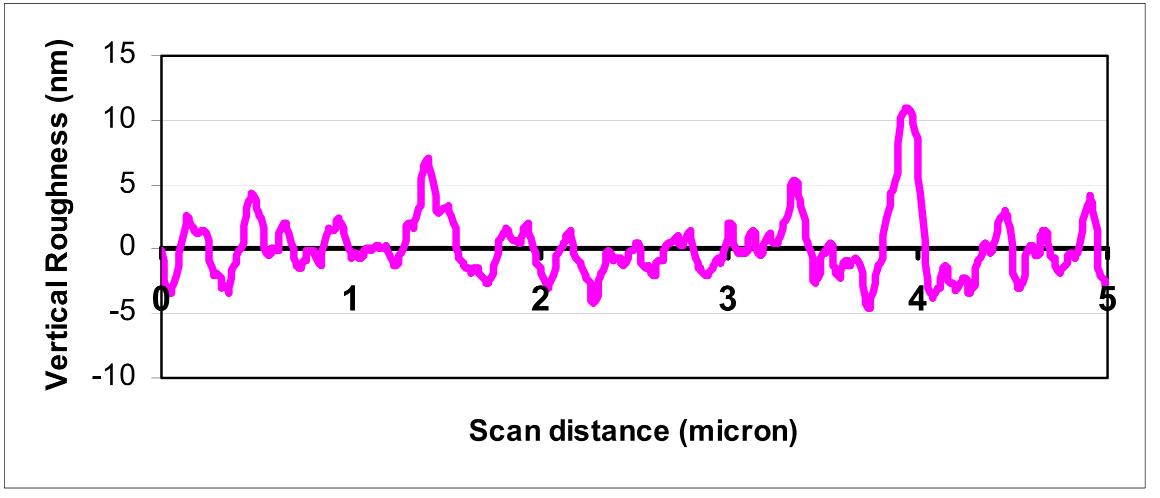
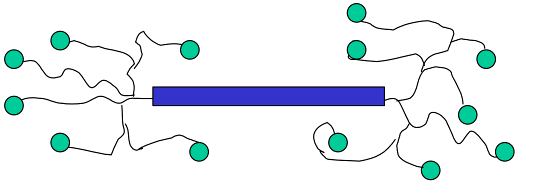
Hyperbranched Copolymers: Surface Roughness

Contact Mode AFM: dry film on float glass





RMS Roughness = 3.9 nm

Film cast at 3000 RPM

No annealing needed

Surface Resistivity = 6,600 Ω/sq.

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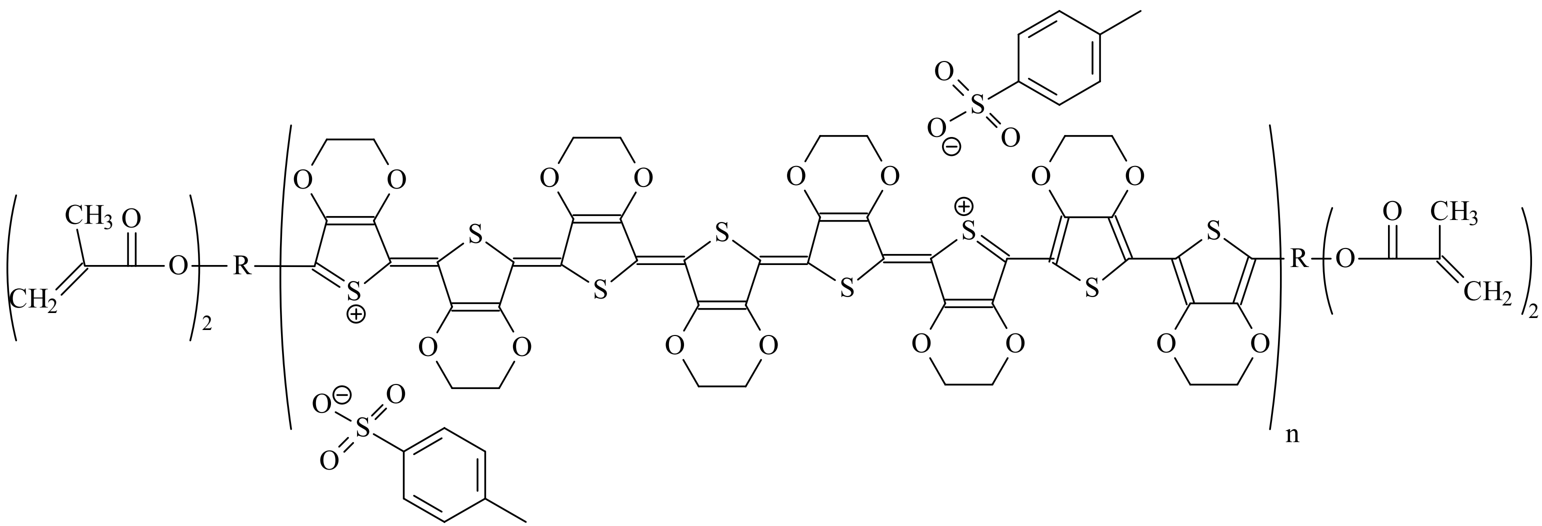
Methacrylated Capped Oligomers



- **Post-curing cross-linking for:**
  - Photo-lithographic patterning
  - Improved scratch resistance
  - Post-inkjet print curing
- **Added functionality for reaction with specific functional compounds**
- **Bulk conductivity = 10^{-2}-10^{0} S/cm (PTSA doped)**

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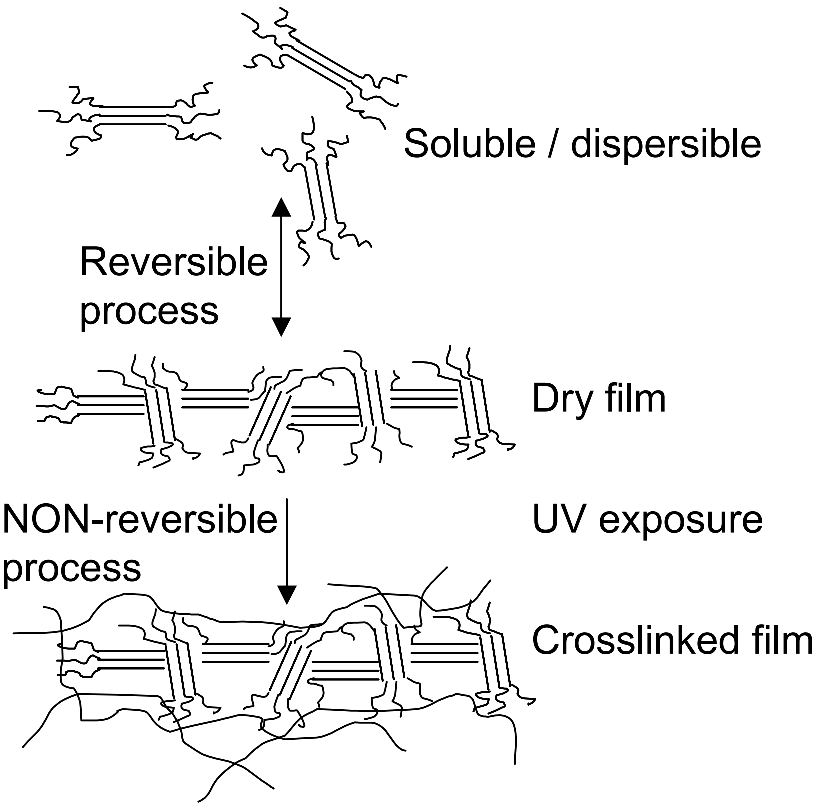
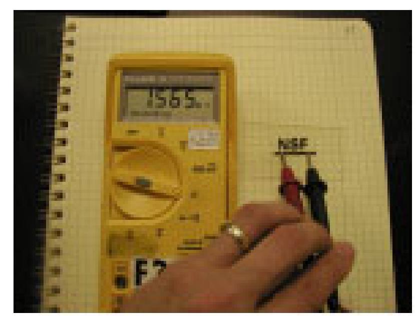
Photoprinting of Methacrylated Oligomers



Areas that are exposed to the light become "fixed" and the rest of the film can be rinsed away

Ink (above), mask (middle) and printed image (bottom)



The printable conducting ink contains a mixture of our conducting polymer and other polymerizable monomers.

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Commercial Products

1. **Aedotron™ C polymer**: Linear PEDOT-PEG/ClO_4 in nitromethane (64980-5)
2. **Aedotron™ C polymer**: Linear PEDOT-PEG/ClO_4 in propylene carbonate (64978-3)
3. **Aedotron™ P polymer**: Linear PEDOT-PEG/PTSA in nitromethane (64979-1)
4. **Oligotron™ material**: PEDOT-tetramethacrylate/PTSA in propylene carbonate (64981-3)
5. **Oligotron™ material**: PEDOT-tetramethacrylate/PTSA in nitromethane (64982-1)

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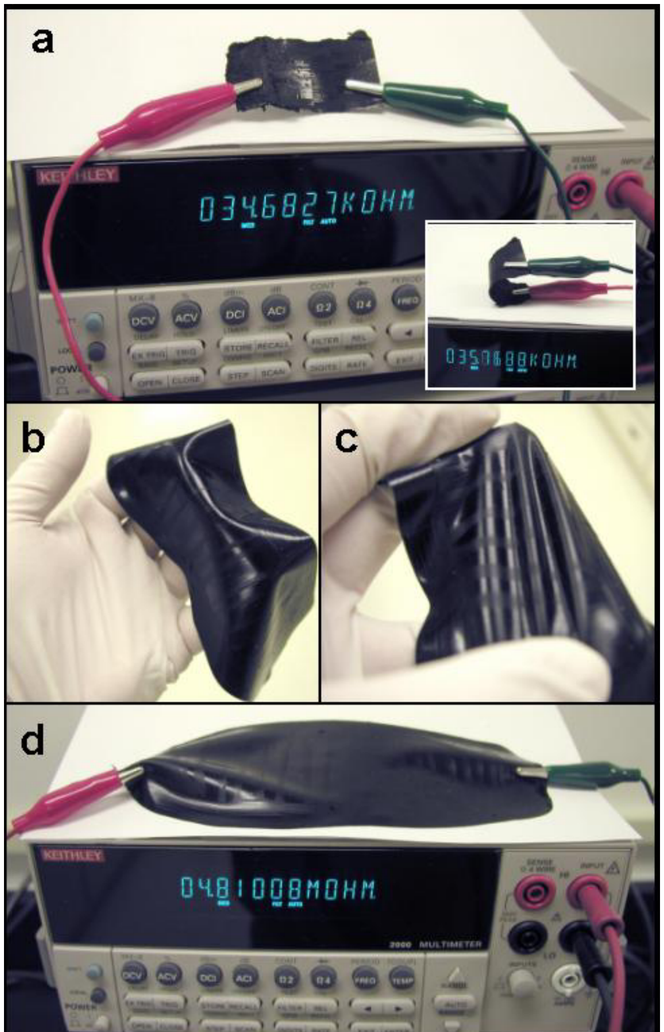
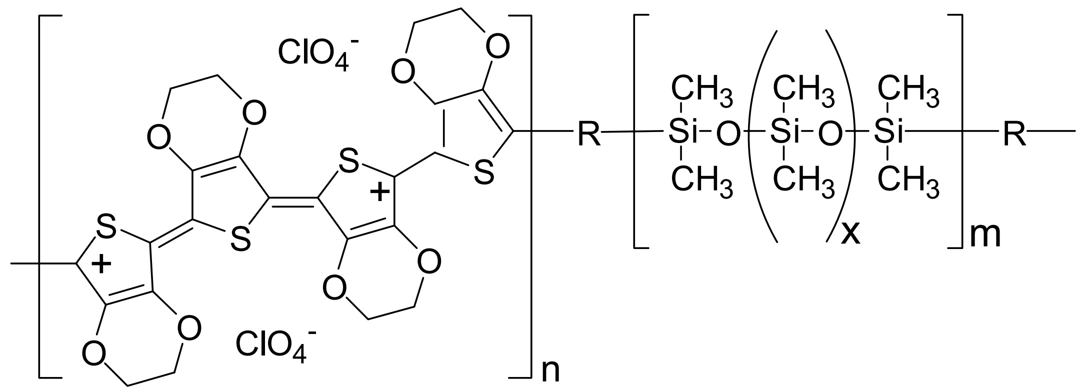
PDMS-PEDOT Copolymers





Conductivity = 10^{-2}-10^{0} S/cm

Elongation = 80-190%

Tensile Strength = 60-100 psi

Glass Transition = -50 °C

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Advantages of TDA's Materials

- Processable from non-acidic organic dispersions
  - ❍ **No ITO etching** ❍ **Not hygroscopic**
- Wet glass and organic substrates
- Conductivity from 10^{-4} to 10 S/cm
  - ❍ **PEDOT/PEG ratio** ❍ **Dopant**
- Colloidal dispersion independent from dopant
- Hyperbranched oligomers have improved conductivity/transparency and lower surface roughness
- Methacryated materials can be cross-linked
- PDMS-PEDOT materials show high conductivity and elongation